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# Structure and electrical properties of $(1-x)(0.1\text{BiYbO}_3-0.9\text{PbTiO}_3)-x\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ high-temperature ternary piezoelectric ceramics

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## ABSTRACT

The microstructure and electrical properties of a new ternary high temperature piezoelectric ceramic system  $(1-x)(0.1\text{BiYbO}_3-0.9\text{PbTiO}_3)-x\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (BYPT–PZN,  $x=0.05-0.5$ ) were reported. The ternary system had a perovskite main phase with a tetragonal symmetry. With increasing PZN content, the tetragonality decreased, and interestingly, both the piezoelectric properties and mechanical quality factor of the samples were largely improved. Microstructural characteristics indicated that the improved piezoelectric performance was also due to the improved density, structural stability and homogeneity. The sample with 40 mol% of PZN ( $x=0.4$ ) showed the optimum piezoelectric response and a  $T_c$  of around 400 °C. However, direct high temperature  $d_{33}$  measurement via the Berlincourt method indicated that depolarization in the sample did not occur up to 350 °C.

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## 1. Introduction

The expanding demand for piezoelectric sensors and actuators working at elevated temperatures, particularly those for aerospace and automotive industries, has motivated a great deal of research interest on piezoelectric ceramics with a Curie temperature ( $T_c$ ) higher than that of the prevalent PZT ( $T_c \approx 320-370$  °C). Piezoelectric materials with a higher  $T_c$  usually show a worse piezoelectric response [1]. While the perovskite solid solution  $(1-x)\text{BiScO}_3-x\text{PbTiO}_3$  (BSPT) shows both a high  $T_c$  of  $\sim 450$  °C and a high  $d_{33}$  of  $\sim 460$  pC/N near the morphotropic phase boundary (MPB) at  $x=0.64$  [2]. High  $T_c$  and high piezoelectric response were also achieved for similar perovskite systems with the general form  $\text{BiMeO}_3-\text{PbTiO}_3$  (BMePT), where Me can be a single or mixture of cations with an average valence of +3. Because of the high cost of  $\text{Sc}_2\text{O}_3$  and the low mechanical quality factor ( $Q_m$ ) of BMePT, scandium-free complex perovskite high temperature piezoelectric ceramics with improved  $Q_m$  are highly desirable [3,4]. A certain lead free system also shows both a high  $T_c$  (about 420) and a high  $d_{33}$  ( $\sim 200$  pC/N) [5], while the evaporation of Na or K during sintering makes it rather difficult to get dense products with stable performance.

Among the BMePT type piezoelectric ceramics,  $\text{BiYbO}_3-\text{PbTiO}_3$  (BYPT) has a high  $T_c$  up to 630 °C. This may be due to its rather low tolerance factor [2,6]. However, it has a low  $d_{33}$  ( $\sim 28$  pC/N), and the large difference in tolerance factor of BY ( $\sim 0.863$ ) and PT (1.02) causes a low solubility of BY in the composite system (less than 10 mol%), leading to difficulties in fabrication [7]. To improve the material stability and the piezoelectric properties, we added PZN (a typical relaxor with a moderate tolerance factor of 0.986) to BYPT and fabricated a new high temperature  $(1-x)(0.1\text{BiYbO}_3-0.9\text{PbTiO}_3)-x\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$  [(1-x)BYPT-xPZN] ternary system. In this study, the microstructure and electrical properties of this new system were reported.

## 2. Experimental

The  $(1-x)\text{BYPT}-x\text{PZN}$  ( $x$  is in the range of 0.05–0.5) ceramics were prepared by the columbite precursor method. The  $\text{ZnNb}_2\text{O}_6$  precursor was mixed with analytically pure  $\text{Bi}_2\text{O}_3$ ,  $\text{Yb}_2\text{O}_3$ ,  $\text{PbO}$  and  $\text{TiO}_2$  according to the stoichiometric ratio (with 1 wt% excess amounts of  $\text{PbO}$ ) and ball-milled, dried, ground, and calcined at 750 °C for 2 h. The final powders were pressed into pellets with a diameter of 12 mm and a thickness of  $\sim 1.2$  mm. Ceramic samples were obtained after sintering at 1100 °C in an sealed crucible. X-ray diffraction (XRD) patterns were recorded by a Bruker D8 Advance diffractometer with  $\text{Cu K}\alpha 1$  radiation. The morphology of the fractured samples was examined by scanning electron microscopy (SEM). The temperature dependence of dielectric constant  $\epsilon_r$

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(1 kHz) of unpoled samples with silver electrodes were measured using an HP4294A impedance analyzer. The high temperature  $d_{33}$  was directly measured by a modified ZJ-3DHT quasistatic piezoelectric type  $d_{33}$ -meter (Institute of Acoustics, Chinese Academy of Sciences) equipped with a high temperature sample chamber and a Pt/Rh thermocouple. The planar electromechanical coupling factor ( $k_p$ ) and the  $Q_m$  were measured by using the resonance and anti-resonance method.

### 3. Results and discussion

The XRD patterns (Fig. 1a) of all samples show a perovskite main phase. The patterns correspond well to the  $\text{PbTiO}_3$  (PDF#70-0746) phase with a typical tetragonal symmetry, showing splitted (001)/(100), (101)/(110), (002)/(200) and (112)/(211) peaks. For the samples with an  $x$  value of 0.05 and 0.1, impurity  $\text{Yb}_2\text{Ti}_2\text{O}_7$  (PDF#17-0454) pyrochlore phase can be identified. When  $x$  is increased to 0.2 and 0.3, the  $\text{Yb}_2\text{Ti}_2\text{O}_7$  phase disappears while  $\text{YbNbTiO}_6$  (PDF#20-1434) and  $\text{PbO}$  (PDF#35-1482) phases are present. The presence of  $\text{PbO}$  may be due to the decomposition of  $\text{PbTiO}_3$  when the sintering temperature is higher than  $890^\circ$  [8]. When  $x$  is further increased to 0.4, the impurity phase changes to  $\text{Pb}_2\text{Ti}_2\text{O}_6$  (PDF#26-0142) pyrochlore phase. For a higher  $x$  of 0.5, more amount of  $\text{Pb}_2\text{Ti}_2\text{O}_6$  is formed. Relatively purer perovskite phase seems to be obtained for an  $x$  value of about 0.4, although impurity phases are hard to be removed completely. With increasing PZN content, the two peaks in each group of the tetragonal

phase patterns approach each other, indicating a decreased tetragonality (lattice parameter ratio  $c/a$ ). The  $x$  dependence of tetragonality derived from the XRD patterns is shown in Fig. 1b. The 0.95BYPT–0.05PZN sample has a tetragonality (1.065) even higher than that of PT (1.063). With increasing  $x$ , the tetragonality shows a decreasing trend and drops to 1.0409 at  $x=0.5$ . A higher tetragonality generally means a higher polarization and lattice deformation, while it may cause difficulty in polarization reversal [9]. Therefore, a suitable tetragonality is important for a high piezoelectric performance.

SEM images of two typical samples with the lowest ( $x=0.05$ ) and the highest content ( $x=0.5$ ) of PZN are shown in Fig. 1c. The morphologies of other samples just have a transitional feature and hence not shown. With increasing PZN content, a loose morphology consisting of irregularly shaped small grains gradually changes to a dense one consisting of grains with sharper boundaries (the density data are shown in Fig. 2b). In addition, the grain size increases substantially from  $\sim 0.5 \mu\text{m}$  at  $x$  of 0.05 to around  $\sim 3\text{--}4 \mu\text{m}$  at  $x$  of 0.5, indicating an enhanced atom mobility and grain growth rate after addition of PZN. The lower image of Fig. 1c also indicates that homogeneous BYPT–PZN solid solution is formed with a high content of PZN.

With increasing PZN content (Fig. 2), both  $d_{33}$  and  $k_p$  values increase substantially and reach a maximum at  $x=0.4$ . Particularly, the  $d_{33}$  is increased for about 6 times from 16 pC/N to 94 pC/N (at  $x=0.4$ ). Generally,  $d_{33}$  and  $Q_m$  show a tradeoff relationship. However, here the  $x$  dependence of  $Q_m$  shows a similar increasing trend as that of  $d_{33}$ , and the maximum  $Q_m$  was increased

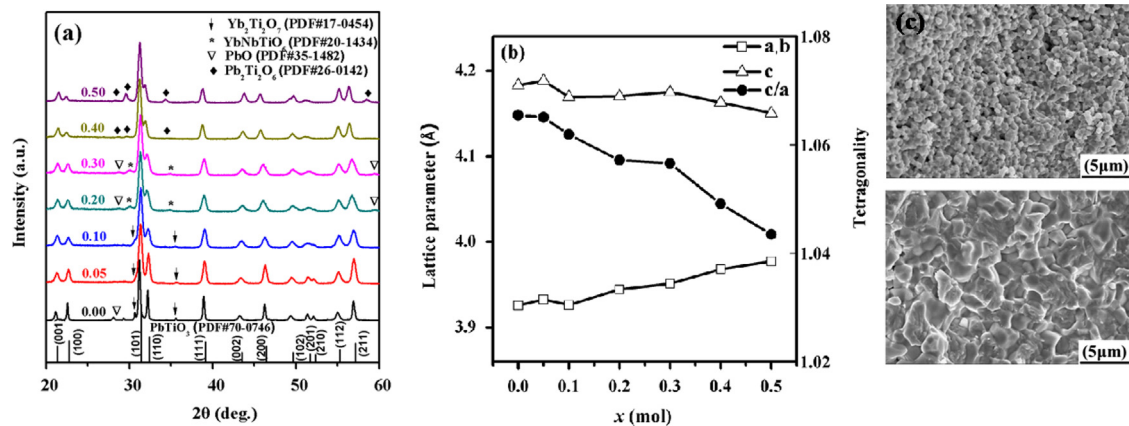


Fig. 1. (a) XRD patterns of various  $(1-x)$ BYPT– $x$ PZN ceramic samples; (b)  $x$  dependence of lattice constants and tetragonality; and (c) SEM images showing the morphology of two typical samples:  $x=0.05$  (upper) and  $x=0.40$  (lower).

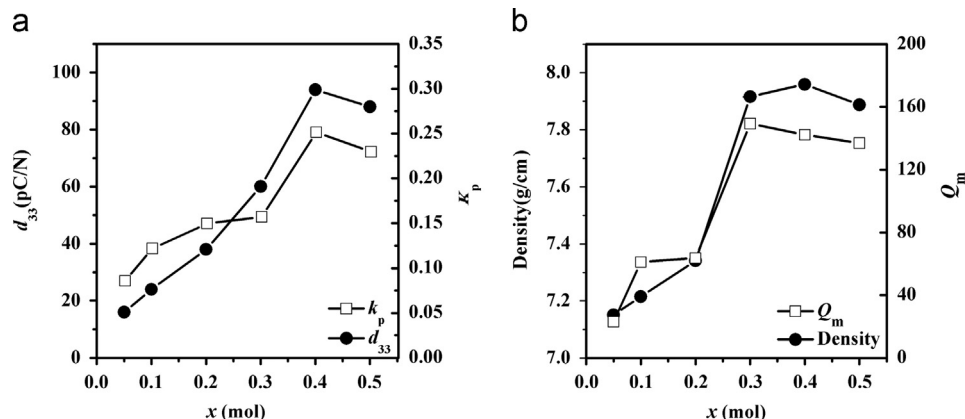


Fig. 2. Some electric parameters and density data of various  $(1-x)$ BYPT– $x$ PZN ceramic samples. (a)  $x$  dependence of piezoelectric coefficient  $d_{33}$  and  $k_p$ , (b)  $x$  dependence of  $Q_m$  and density.

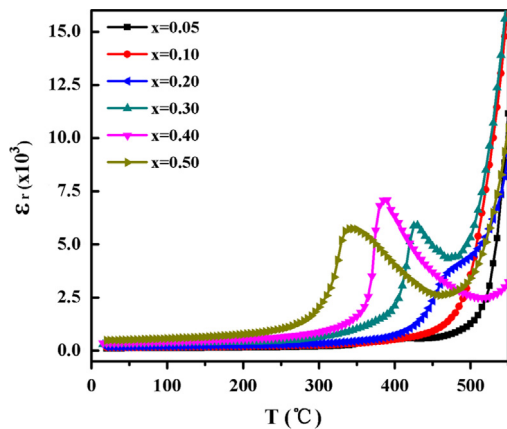


Fig. 3. Temperature dependence of dielectric constant ( $\epsilon_r$ ) (1 kHz) for various  $(1-x)$ BYPT- $x$ PZN ceramic samples.

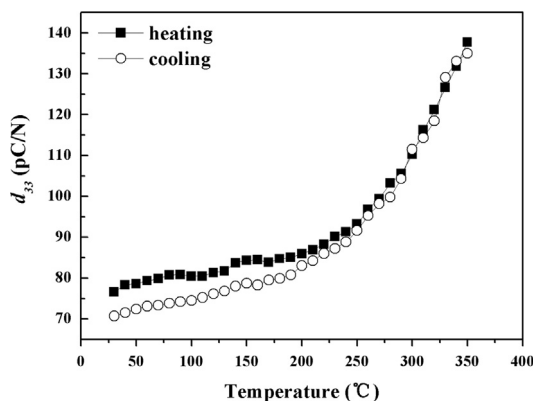


Fig. 4. Temperature dependence of  $d_{33}$  directly measured from the Berlincourt method of the sample having the highest piezoelectric response (0.6BYPT-0.4PZN).

substantially to about 150. This might be partly explained by the increased density (Fig. 2b), because a dense structure may reduce the dissipated energy and improve the piezoelectric response as well. Also, combining the SEM and the XRD results, one can find that the sample with the highest  $d_{33}$  (at  $x=0.4$ ) shows relatively purer perovskite phase and more homogeneous morphology. Therefore, the improved piezoelectric performance may be partly attributed to the improved structural stability and homogeneity. It may also be attributed to the decreased tetragonality, because a lower tetragonality may facilitate domain switching and off-center displacement of the B-site ions.

The temperature dependence of dielectric constant ( $\epsilon_r$ ) is shown in Fig. 3. For the sample with an  $x$  value of 0.05, 0.1 and 0.2, the  $\epsilon_r$  curves show no anomaly in the tested temperature range. When  $x$  is higher than 0.2, the peak due to ferroelectric-paraelectric phase transition appears, and the corresponding  $T_c$

decreases with increasing  $x$ . The sample with the highest PZN ratio of 0.5 shows a diffused phase transition. The decrease in  $T_c$  with increasing PZN content may be explained by the decreased tetragonality [10].

Fig. 4 shows the high temperature  $d_{33}$  of the 0.6BYPT-0.4PZN sample directly measured by the  $d_{33}$  meter based on the Berlincourt method. The reported depolarization temperature of BSPT is around 330 °C [11]. However, repeated measurements show that the  $d_{33}$  of the sample increases monotonously, and depolarization does not occur in the tested temperature range (RT-350 °C) despite its much lower  $T_c$  than that of BSPT or BSPT-PZN. This also implies that the nominal  $T_c$  is not always suitable to evaluate the depolarization behaviors. Further work is on-going to elucidate the details and to improve the piezoelectric performance.

#### 4. Conclusions

Incorporation of PZN to BYPT largely improves the piezoelectric response and the  $Q_m$  of the ternary  $(1-x)$ BYPT- $x$ PZN system. The improved piezoelectric performance is also attributed to the improved perovskite phase stability and structural homogeneity with decreased tetragonality. More importantly, the depolarization temperature of this new system was found to be higher than 350 °C, although the  $T_c$  is around 400 °C.

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